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(71) Applicant *(for all designated States except US)*: **ABB AB** [SE/SE]; S-721 83 Västerås (SE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ISBERG, Peter** [SE/SE]; Lindskärsv. 15, S-725 92 Västerås (SE). **PALMQUIST, Jens-Petter** [SE/SE]; Blodstensvägen 29, S-758 58 Uppsala (SE). **JANSSON, Ulf** [SE/SE]; Uppsala Universitet, The Ångström Laboratory, Lägerhyddsvägen 1, S-751 21 Uppsala (SE). **HULTMAN, Lars** [SE/SE]; Linköping, Uvebergsv. 20, S-589 31 Linköping (SE). **BIRCH, Jens** [SE/SE]; Fanjunkareg. 115, S-582 16 Linköping (SE). **SEPPÄNEN, Timo** [SE/SE]; Syréngatan 10a, S-582 46 Linköping (SE).

(74) Agent: **ABB GROUP SERVICES CENTER AB**; Legal & Compliance/ Intellectual Property, Forskargränd 8, S-721 78 Västerås (SE).

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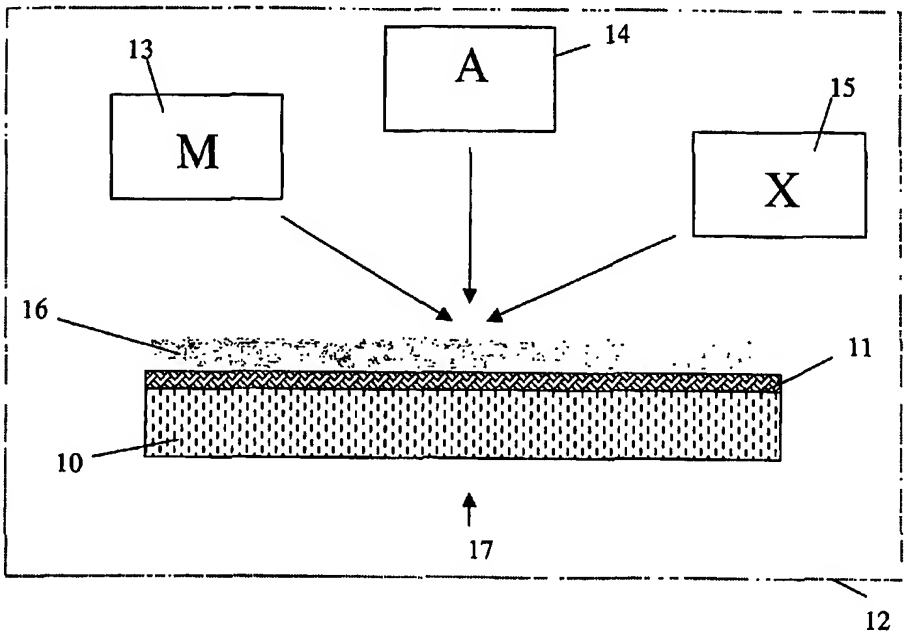
(54) Title: METHOD OF SYNTHESIZING A COMPOUND OF THE FORMULA $M_{n+1}AX_n$, FILM OF THE COMPOUND AND ITS USE




(57) Abstract: A method of synthesizing or growing a compound having the general formula $M_{n+1}AX_n$(16) where M is a transition metal, n is 1, 2, 3 or higher, A is an A-group element and X is carbon, nitrogen or both, which comprises the step of exposing a substrate to gaseous components and/or components vaporized from at least one solid source (13, 14, 15) whereby said components react with each other to produce the $M_{n+1}AX_n$ (16) compound.

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METHOD OF SYNTHESIZING A COMPOUND OF THE FORMULA $M_{n+1}AX_n$, FILM OF THE COMPOUND AND ITS USE

The present invention relates to a method of synthesizing or growing a compound having the general formula $M_{n+1}AX_n$, where M is at least one transition metal, n is 1, 2, 3 or higher, A is at least one A-group element and X is carbon or nitrogen, or both carbon and nitrogen.

## BACKGROUND OF THE INVENTION

Recent studies have shown that ternary and quaternary compounds having the general formula $M_{n+1}AX_n$ exhibit unusual and exceptional mechanical properties as well as advantageous electrical, thermal and chemical properties. Despite having high stiffness these ceramics are readily machinable, resistant to thermal shock, unusually damage tolerant, have low density and are thermodynamically stable at high temperatures (up to 2300°C).

$M_{n+1}AX_n$ compounds have layered and hexagonal structures with $M_2X$ layers interleaved with layers of pure A and it is this structure, comprising exceptionally strong "metallic" M-X bonds together with relatively weak M-A bonds, which gives rise to their unusual combination of properties.

$M_{n+1}AX_n$ compounds are characterized according to the number of transition metal layers separating the A-group element layers: in "211" compounds there are two such transition metal layers, in "312" compounds there are three and in "413" compounds there are four. 211 compounds are the most predominant, these include $Ti_2AlC$, $Ti_2AlN$, $Hf_2PbC$, $Nb_2AlC$, $(Nb,Ti)_2AlC$, $Ti_2AlN_{0.5}C_{0.5}$, $Ti_2GeC$, $Zr_2SnC$, $Ta_2GaC$, $Hf_2SnC$, $Ti_2SnC$, $Nb_2SnC$, $Zr_2PbC$ and $Ti_2PbC$. The only known 312 compounds are $Ti_3AlC_2$,

$Ti_3GeC_2$, $Ti_3SiC_2$. $Ti_4AlN_3$ and $Ti_4SiC_3$ are the only 413 compound known to exist at present. A very large number of solid solution permutations and combinations are also conceivable as it is possible to form solid solutions on the M-sites, the A-sites and the X-sites of these different phases.

Michel Barsoum has synthesized, characterized and published data on the $M_{n+1}AX_n$ phases named above in bulk form ["The $M_{n+1}AX_n$ Phases: A New Class of Solids", Progressive Solid State Chemistry, Vol. 28 pp201-281, 2000]. His measurements on $Ti_3AlC_2$ show that it has a significantly higher thermal conductivity and a much lower electrical resistivity than titanium and, like other $M_{n+1}AX_n$ phases, it has the ability to contain and confine damage to a small area thus preventing/limiting crack propagation through the material. Its layered structure and the fact that bonding between the layers is weaker than along the layers (as in graphite) give rise to a very low friction coefficient, even after six months exposure to the atmosphere. Polycrystalline samples however do not have such a low friction coefficient and tend to be brittle at room temperature.

Barsoum's synthesis process, for the $M_{n+1}AX_n$ phases he studied, involved the simultaneous application of high temperature and high pressure to starting materials in bulk form in a hot isostatic press. The starting materials react under pressure to produce $M_{n+1}AX_n$ phases. The methods used for producing epitaxial binary carbide films (such as chemical vapour deposition, CVD and physical vapour deposition, PVD) are carried out at high temperatures (1000-1400°C). Films grown or synthesized at lower temperatures tend to be amorphous or compact grained. As yet there is no method that is able to produce crystalline/epitaxial thin films or coatings of $M_{n+1}AX_n$ at a relatively low temperature.

## SUMMARY OF THE INVENTION

It is an object of this invention to synthesize or grow a compound having the general formula $M_{n+1}AX_n$ where M is at least one transition metal, n is 1, 2, 3 or higher, A is at least one A-group element and X is carbon, nitrogen or both, in the form of thin films or coatings.

This and other objects of the invention are achieved by utilizing a method that comprises the step of exposing a substrate to gaseous components and/or components vaporized from at least one solid source whereby said components react with each other to produce the $M_{n+1}AX_n$ compound. In a preferred embodiment of the invention the method comprises the step of vaporizing at least one transition metal, at least one A-group element and at least one X element from at least one source.

According to a further preferred embodiment of the invention the substrate comprises one of the following materials: a metal, such as copper, aluminium, nickel or gold, a non-metal, a semiconductor such as GaAs, a ceramic, a polymer, an oxide, a binary metal carbide, nitride or carbonitride, a $M_{n+1}AX_n$ compound, MgO, SiC, oriented graphite, $C_{60}$, sapphire or silicon.

In another preferred embodiment of the invention the substrate comprises a seed layer (i.e. buffer layer, template layer, nucleation layer) on which the $M_{n+1}AX_n$ compound is synthesized or grown. The seed layer is produced by any suitable means either ex-situ or in situ or by a combination of both ex situ and in situ steps. This means that a suitable seed layer is produced prior to carrying out the method of the present invention, or it is produced in situ prior to synthesizing or growing the $M_{n+1}AX_n$ compound, or a previously applied surface component is treated and thus modified in situ to promote the nucleation, formation or growth of the $M_{n+1}AX_n$ compound. According to

a preferred embodiment of the invention the seed layer comprises a material exhibiting an epitaxial relationship or a preferred crystallographic orientation to the $M_{n+1}AX_n$ compound to be synthesized. In a preferred embodiment the seed layer comprises a transition metal carbide or nitride or carbonitride for example titanium carbide or titanium nitride, oriented graphite, $C_{60}$ or at least one of the components of the $M_{n+1}AX_n$ compound.

According to another preferred embodiment of the invention the components required to produce the seed layer and/or the $M_{n+1}AX_n$ compound are vaporized from at least one solid source by physical vapour deposition. In a further preferred embodiment of the invention at least one of the components required to produce the seed layer and/or the $M_{n+1}AX_n$ compound is vaporized from a $M_{n+1}AX_n$ target.

According to a preferred embodiment of the invention, where carbon is required, the carbon source is either solid, for example high purity graphite, or gaseous, for example a hydrocarbon gas. In a further preferred embodiment of the invention it comprises at least one of the following nanostructures: buckyballs; $C_{60}$, $C_{70}$, nanotubes, nanoropes, nanofibres, azafullerenes or any other carbon nanostructures having a diameter between 0.1 and 100 nm. Such nanostructures may be formed from carbon sources or suitable precursors by an electric arc process, sputtering, catalytic pyrolysis, electron beam evaporation, vaporization or laser ablation. In another preferred embodiment the carbon source comprises doped nanostructures in order to modify the chemical composition of the subsequently produced $M_{n+1}AX_n$ and thereby its mechanical, electrical or thermal properties.

According to other preferred embodiments of the invention an atomic flow of carbon is obtained using a PVD process or from a carbon-containing gas such as a hydrocarbon. In another preferred embodiment of the invention

the carbon source is produced from a suitable precursor such as metal-fullerene nanoclusters.

The composition and crystallinity of the $M_{n+1}AX_n$ compound formed on the substrate is controlled by the ratio of the components reaching the substrate, the seed layer used, and the temperature of the substrate. The method of the present invention renders relatively low substrate temperatures possible due the highly reactive atomic state of the components that form the $M_{n+1}AX_n$ compound and the high purity of the carbon sources used. This means for example that epitaxial films can be obtained at relatively low temperatures.

In a preferred embodiment of the invention the substrate is heated to a temperature between room temperature and 1400°C, preferably 800°C or lower. According to a yet further preferred embodiment of the invention the temperature to which said substrate is heated is changed while the $M_{n+1}AX_n$ compound is being grown. Alternatively the substrate surface is treated with plasma or bombarded with energetic particles such as ions, electrons, neutral atoms, molecules or clusters to promote growth of the seed layer.

In a preferred embodiment of the invention the method comprises the further step of periodically changing the nature or the ratio of the components supplied to the nucleation surface. By "nature of the components" it is meant that the M, A and/or X components used are changed to give rise to a structure comprising a combination of different $M_{n+1}AX_n$ compounds. For example the nature or ratio of the components is changed in a stepwise manner to produce a laminate with distinct layers of the same or different $M_{n+1}AX_n$ compound(s) and layers of materials (M) such as metals, binary carbides or nitrides. For example the nature or ratio of components supplied to said substrate is changed alternately in order to

produce a multi-layer laminate comprising alternate layers of a $M_{n+1}AX_n$ compound and layers of materials such as metals, $M_{n+1}AX_n$ compounds, binary carbides or nitrides.

Laminates having the following structures, as well as permutations of these structures can be easily produced:

$M / M_{n+1}AX_n / M / M_{n+1}AX_n / M / M_{n+1}AX_n / M$...etc.

$MX / M_{n+1}AX_n / MX / M_{n+1}AX_n / MX / M_{n+1}AX_n / MX$...etc.

$AX / M_{n+1}AX_n / AX / M_{n+1}AX_n / AX / M_{n+1}AX_n / AX$...etc.

An alternating metal-$M_{n+1}AX_n$ structure can, for example, be achieved by alternately breaking off the flow of the carbon and A-group components to the substrate.

Alternatively the method of the present invention comprises the further step of *gradually* changing the nature or the ratio of the components supplied to the substrate in order to produce a graded laminate. The method of the present invention is carried out in a vacuum, noble gas, nitrogen- or carbon-containing gas atmosphere.

This method is intended for the synthesis or growth of both epitaxial and non-epitaxial compounds i.e. where the $M_{n+1}AX_n$ layer synthesized/grown exhibits an epitaxial relationship or preferred crystallographic orientation to grains in a substrate, a seed layer or to a single crystal substrate. The method described can be used to produce thin films that are one $M_{n+1}AX_n$ crystallographic unit cell to a few millimeters thick.

Such a method is suitable for used in the manufacture of electric contacts, films or coatings having a low coefficient of friction, anti-stick-films, lubricating films or coatings in micromechanics or catalytically active films. It can be used for the manufacture of protective films or coatings that are at

least one of the following corrosion-resistant, thermally stable, wear resistant, impact resistant or oxidation resistant

$M_{n+1}AX_n$ compounds are capable of supporting an external load or further film deposition such as metallisation. They are suitable as coatings for devices in applications where dimensional stability under rotation or translation is important such as in disk drives and sensor heads. They can be used as lubricating films or coatings in micro-mechanical applications for example on hard disks.

They are also suitable as coatings for commutating brushes for DC motors and applications where contact surfaces move while bearing against each other in establishing and/or breaking electrical contact such as in circuit spring-loaded contacts in circuit breakers or spring contacts to printed circuit boards. Due to the low friction coefficient of these materials, the friction forces to be overcome when establishing or breaking electric contact will be very low which means that power consumption will be low and the wear on the contact surfaces will be negligible. They are equally suitable as surface coatings for cutting tools as they provide a wear resistant, hard and impact resistant surface that does not require lubrication or cooling while cutting.

## BRIEF DESCRIPTION OF THE DRAWING

A greater understanding of the present invention may be obtained by reference to the accompanying drawing, when considered in conjunction with the subsequent description of the preferred embodiments, in which

figure 1 is a schematic representation of the method of the present invention,

figure 2 depicts a structure produced using the method according to present invention, and

figure 3 shows an X-ray diffraction pattern of a $Ti_3SiC_2$ layer of approximately 100 nm thickness deposited on a TiC (111) seed layer on a MgO (111) substrate.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 shows a substrate 10, comprising a seed layer 11, contained in a vacuum chamber 12. The substrate with the seed layer is exposed to at least one transition metal (M), such as titanium or two transition metals such as titanium and vanadium, vaporized from a solid source 13, at least one A-group element (A) vaporized from a solid source 14 and carbon produced from by vaporization of a carbon source 15. The carbon source may for example comprise high-purity graphite, nanostructures or optionally doped nanostructures such as metal-fullerene clusters.

The transition metal and A-group element sources can be vaporized by a physical vapour deposition method for example. PVD processes involve the evaporation of at least one of the reactants in a high vacuum chamber ($10^{-3}$ to $10^{-6}$ mbar) by heating, sputtering or arc-evaporation. PVD methods include laser ablation in which a high-energy laser blasts material from a target and through a vapour to the substrate where the material is deposited. Other PVD approaches are sputter and arc deposition in which energetic ions bombard the surface of a target, generating a flux of target atoms.

The M, A and X components react with each other produce a compound having the general formula $M_{n+1}AX_n$, 16. A thin layer of $M_{n+1}AX_n$ is formed having an epitaxial or a non-epitaxial relationship with the seed layer 11 or

another relationship favourable for the formation of said compound. The substrate 10 is heated 17 to the temperature conducive to the formation of the $M_{n+1}AX_n$ compound having the properties required in the as-deposited state or after subsequent processing. In the production of a film comprising at least one epitaxial layer of $Ti_3SiC_2$ for example, the substrate can be MgO and the seed layer can be TiC.

Figure 2 shows a laminate having alternating metal carbide layers (18), TiC for example and $M_{n+1}AX_n$, 16 layers. Such a structure is obtainable using the method of the present invention by periodically stopping the flow A components so as to form the metal carbide layers. The composition of the $M_{n+1}AX_n$ layers may be controlled by changing the ratio of the components reaching the substrate for example by changing the rate of evaporation from the carbon source or the power of a vaporization laser used to produce the one or more of the components. The properties of such a multi-layer structure will depend not only on the composition of the layers but also on the crystal structure and thickness of the layers. The non-$M_{n+1}AX_n$ layers 18 of such a laminate do not have to contain a binary metal carbide as in this example. These layers can comprise metals or metal nitrides, for example. Similarly all of the $M_{n+1}AX_n$ layers 16 do not have to comprise the same $M_{n+1}AX_n$ compound.

Figure 3 shows an X-ray diffraction pattern of an epitaxial $Ti_3SiC_2$ layer of approximately 100nm thickness deposited on a TiC (111) seed layer on a MgO (111) substrate. The graph shows that the $Ti_3SiC_2$ has a 0001 orientation. To the inventors' knowledge the sample that was used to obtain these XRD-results is the first ever epitaxial 312 film.

While only certain preferred features of the present invention have been illustrated and described, many modifications and changes will be apparent to those skilled in the art. It is therefore to be understood that all such

modifications and changes of the present invention fall within the scope of the claims. For example the word "layer" should not be interpreted to mean only deposits that cover an entire surface but is intended to refer to any deposit of $M_{n+1}AX_n$ compound or seed layer material on any part of a surface.

## CLAIMS

1. A method of synthesizing or growing a compound having the general formula $M_{n+1}AX_n$ (16) where M is at least one transition metal, n is 1, 2, 3 or higher, A is at least one A-group element and X is carbon, nitrogen or both, **characterized** in that it comprises the step of exposing a substrate to gaseous components and/or components vaporized from at least one solid source (13, 14, 15) whereby said components react with each other to produce the $M_{n+1}AX_n$ (16) compound.

2. A method according to claim 1, **characterized** in that it comprises the vaporizing of at least one transition metal (13), at least one A-group element (14) and at least one X element (15) from at least one source.

3. A method according to claims 1 or 2, **characterized** in that said substrate (10) comprises one of the following materials: a metal, a non-metal, a semiconductor, a ceramic, a polymer, an oxide, a binary metal carbide, nitride or carbonitride, a $M_{n+1}AX_n$ compound, MgO, SiC, oriented graphite, $C_{60}$ , sapphire or silicon.

4. A method according to any preceding claims, **characterized** in that the substrate comprises a seed layer (11), on which the $M_{n+1}AX_n$ compound (16) is synthesized or grown, which is produced ex situ, in situ or by a combination of both ex situ and in situ steps.

5. A method according to claim 4, **characterized** in that it comprises the step of initially producing a seed layer (11) on the substrate prior to synthesizing or growing the $M_{n+1}AX_n$ compound (16) thereon.

6. A method according to any of claims 4 or 5, **characterized** in that the seed layer comprises a material exhibiting an epitaxial relationship or a preferred crystallographic orientation to the $M_{n+1}AX_n$ compound to be synthesized or grown.

7. A method according to any of claims 4-6, **characterized** in that said seed layer (11) comprises a transition metal carbide or nitride or carbonitride, oriented graphite, $C_{60}$ or at least one component of the $M_{n+1}AX_n$ compound.

8. A method according to any preceding claims, **characterized** in that the components required to produce the seed layer (11) and/or the $M_{n+1}AX_n$ compound (16) are vaporized from at least one solid source (13, 14, 15) by physical vapour deposition.

9. A method according to any of preceding claims, **characterized** in that at least one of the components required to produce the seed layer (11) and/or the $M_{n+1}AX_n$ compound (16) is vaporized from a $M_{n+1}AX_n$ target.

10. A method according to any preceding claims, **characterized** in that, where carbon is required, the carbon source (15) comprises high-purity graphite.

11. A method according to any of claims 1-9, **characterized** in that, where carbon is required, the carbon source (15) is gaseous.

12. A method according to any of claims 1-9, **characterized** in that, where carbon is required, the carbon source (15) comprises at least one of the following nanostructures: buckyballs; $C_{60}$, $C_{70}$, nanotubes, nanoropes, azafullerenes or any other carbon

nanostructure having a diameter between 0.1 and 100 nm.

13. A method according to claim 12, **characterized** in that the carbon source (15) comprises nanostructures that are doped so as to modify the chemical composition of the subsequently produced $M_{n+1}AX_n$ compound (16) and to improve the mechanical, electrical or thermal properties of said compound.

14. A method according to any of claims 1-9, **characterized** in that, where carbon is required, the carbon source (15) is produced from a suitable precursor such as metal-fullerene nanoclusters.

15. A method according to any preceding claims, **characterized** in that said substrate (10) is heated.

16. A method according to claim 13, **characterized** in that said substrate (10) is heated to a temperature of 800°C or lower.

17. A method according to claims 13 or 14, **characterized** in that the temperature to which said substrate (10) is heated is changed while the $M_{n+1}AX_n$ compound is being grown.

18. A method according any of claims 1-14, **characterized** in that said substrate (10) is treated with plasma or bombarded with energetic particles such as ions, electrons, neutral atoms, molecules or clusters.

19. A method according to any preceding claims, **characterized** in that it comprises the further step of periodically changing the nature or the ratio of the components supplied to the nucleation surface to produce a multi-layer laminate comprising layers of (the same or

different) $M_{n+1}AX_n$ compounds (16) and layers of materials (18) such as metals, binary carbides or nitrides.

20. A method according to claim 19, **characterized** in the nature or ratio of components supplied to said substrate is changed alternately in order to produce a multi-layer laminate comprising alternate layers of $M_{n+1}AX_n$ (16) compounds and layers of materials (18) such as metals, $M_{n+1}AX_n$ (16) compounds, binary carbides or nitrides.

21. A method according to any of claims 1-18, **characterized** in that it comprises the further step of gradually changing the nature or the ratio of the components supplied to the substrate in order to produce a graded laminate.

22. A method according to any preceding claims **characterized** in that said method is carried out in a vacuum, noble gas, nitrogen- or carbon-containing gas atmosphere (12).

23. A film, **characterized** in that it comprises at least one epitaxial $M_{n+1}AX_n$ layer.

24. A film, **characterized** in that it comprises at least one non-epitaxial $M_{n+1}AX_n$ layer.

25. A film according to claims 23 or 24, **characterized** in that said $M_{n+1}AX_n$ compound (16) is produced as a film that is one $M_{n+1}AX_n$ crystallographic unit cell to a few millimeters thick.

26. Use of a method according to any of claims 1-22 or a film according to any of claims 23-25 for the manufacture of electric

contacts.

27. Use of a method according to any of claims 1-22 or a film according to any of claims 23-25 for the manufacture of films or coatings having a low coefficient of friction.

28. Use of a method according to any of claims 1-22 or a film according to any of claims 23-25 for the manufacture of lubricating films, anti-stick films or coatings in micromechanics.

29. Use of a method according to any of claims 1-22 or a film according to any of claims 23-25 for the manufacture of protective films or coatings that are at least one of the following corrosion-resistant, thermally stable, wear resistant, impact resistant or oxidation resistant

30. Use of a method according to any of claims 1-22 or a film according to any of claims 23-25 for the manufacture of catalytically active films.

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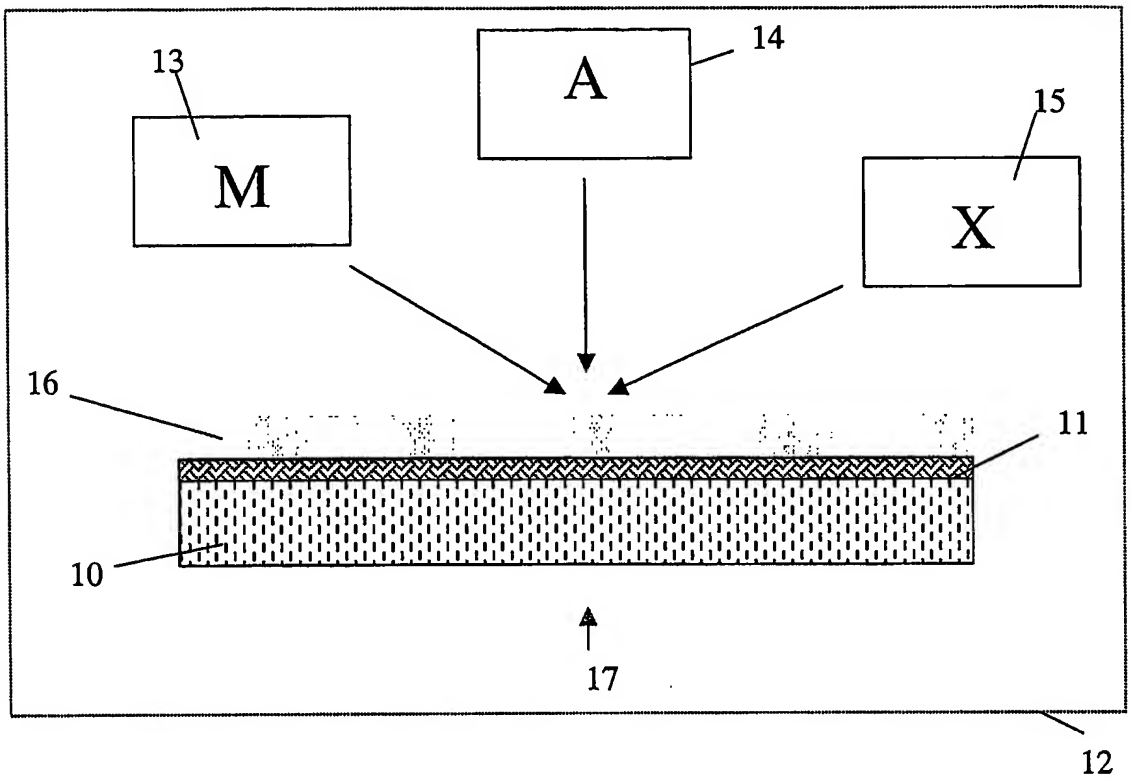


Fig 1

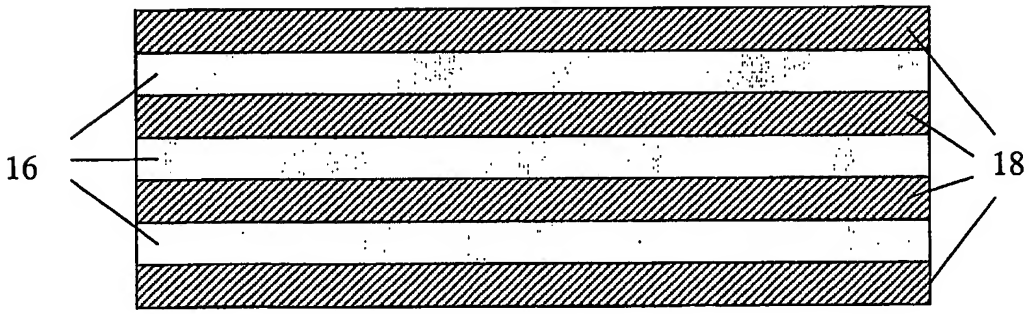


Fig 2

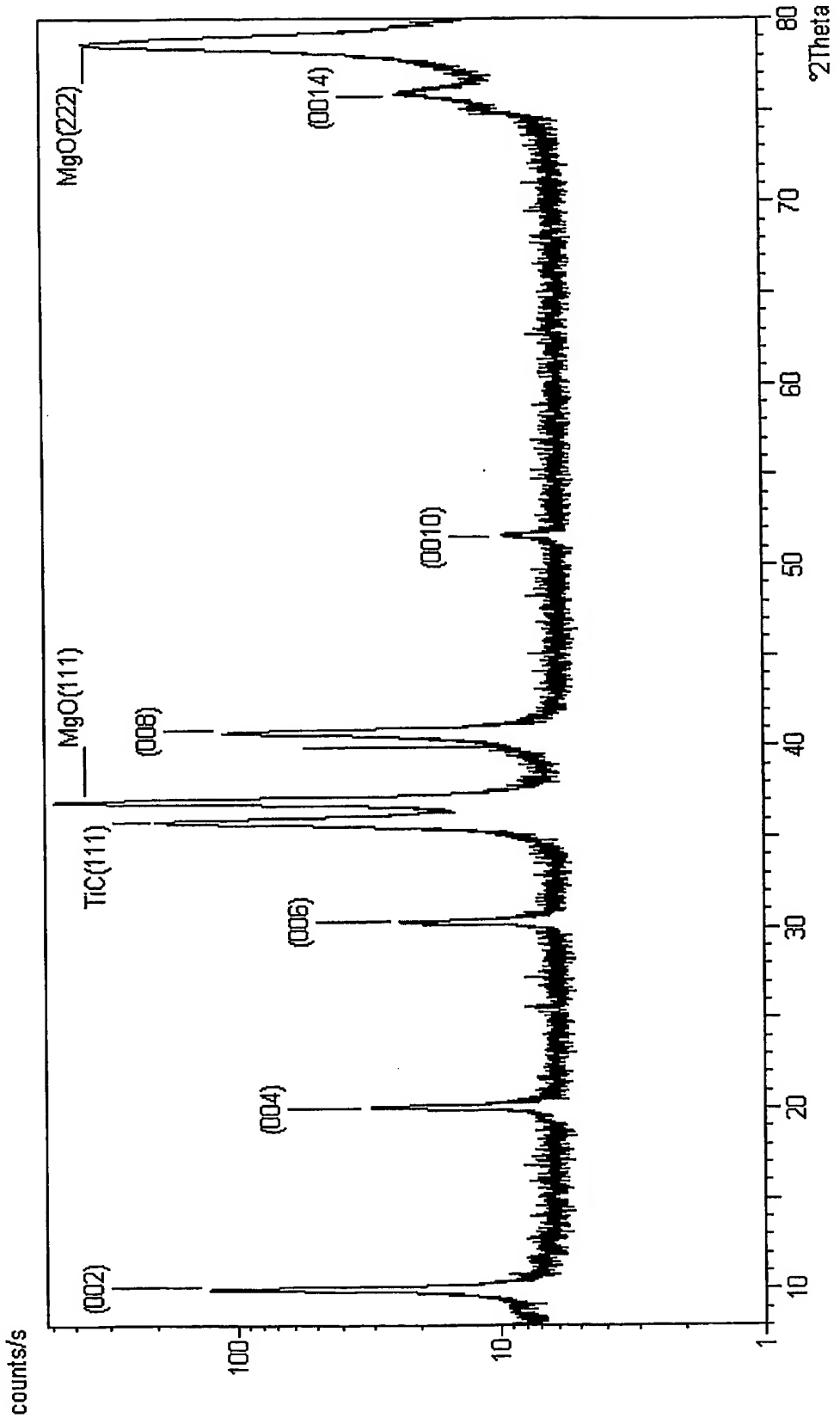
MgO(222)
(0014)
(0010)
(008)
MgO(111)
TiC(111)
(006)
(004)
(002)
counts/s
100
10
1
10
20
30
40
50
60
70
80
°2Theta

Fig 3

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/02215

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C23C 14/06, C30B 28/12, C30B 29/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0448720 A1 (SUMITOMO ELECTRIC INDUSTRIES, LTD.), 2 October 1991 (02.10.91), page 2, line 30 - page 3, line 17; page 3, line 23 - page 5, line 23 | 1-3,8,11,15, 16,18-22,24, 25 |
| A | -- | 4-7,9,10, 12-14,17,23, 26-30 |
| X | Prog Solid St Chem., Volume 28, 2000, Michel W. Barsoum, "The M(N+1)AX(N)Phases: A New Class of Solids; Thermodynamically Stable Nanolaminates(pp 201-281)" page 201 - page 210; page 271 | 1,23,24,25, 26-30 |
| A | -- | 2-22 |

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 February 2003 | 20 -02- 2003 |
| Name and mailing address of the ISA/<br>Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Authorized officer<br>Nils Engnell/MP<br>Telephone No. +46 8 782 25 00 |

Form PCT/ISA/210 (second sheet) (July 1998)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/02215

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | Mat.Res.Bull., Volume 22, 1987, T. Goto et al, "Chemically Vapor Deposited Ti3SiC2 (pp 1195-1201)" | 1,23-25 |
| A | -- | 2-22,26-30 |
| A | EP 0588350 A2 (YOSHIDA KOGYO K.K.), 23 March 1994 (23.03.94) | 1-22,23-25, 26-30 |
| | -- | |
| A | US 6063185 A (CHARLES ERIC HUNTER), 16 May 2000 (16.05.00), column 2, line 49 - column 3, line 46 | 1-22,23-25, 26-30 |
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| A | US 5580653 A (YUSUKE TANAKA ET AL), 3 December 1996 (03.12.96) | 1-22,23-25, 26-30 |
| | -- | |
| | -------- | |

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/02215

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| EP 0448720 A1 | 02/10/91 | SE 0448720 T3 | |
| | | DE 69020719 D,T | 02/11/95 |
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| | | JP 2793773 B | 03/09/98 |
| | | JP 7310174 A | 28/11/95 |

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# PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

# PCT

To:

ABB AB Legal & Compliance/
Intellectual Property
Forskargränd 8
721 78 Västerås
Sverige

Ankom
2005 -04- 20
CF - LC / IP

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

| | |
|---|---|
| Applicant's or agent's file reference<br>9591WO/AT/LA | Date of mailing *(day/month/year)*<br>19 -04- 2005 |
| International application No.<br>PCT/IB2004/003390 | **FOR FURTHER ACTION** See paragraphs 1 and 4 below |
| Applicant<br>ABB Research Ltd<br>et al | International filing date *(day/month/year)*<br>18-10-2004 |

1. [X] The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith. 2005-06-19

   **Filing of amendments and statement under Article 19:**
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   **When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report.

   **Where?** Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 740 14 35

   **For more detailed instructions**, see notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

   [ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

   [ ] no decision has been made yet on the protest: the applicant will be notified as soon as a decision is made.

4. **Reminders**

   Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

   The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

   In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

   See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

| | |
|---|---|
| Name and mailing address of the ISA/<br>Patent- och registreringsverket<br>Box 5055<br>S-102 42 STOCKHOLM<br>Facsimile No. 08-667 72 88<br>Telex 17978 PATOREG-S | Authorized officer<br>Inger Willén<br>Telephone No. 08-782 25 00 |

*(See notes on accompanying sheet)*

Form PCT/ISA/220 (January 2004)

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| Applicant's or agent's file reference 9591WO/AT/LA | FOR FURTHER ACTION | see Form PCT/ISA/220 as well as, where applicable, item 5 below. |
|---|---|---|
| International application No. PCT/IB 2004/003390 | International filing date *(day/month/year)* 18 October 2004 | (Earliest) Priority Date *(day/month/year)* 16 October 2003 |
| Applicant ABB Research Ltd. et al | | |

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II)

3. ☐ **Unity of invention is lacking** (see Box No. III)

4. With regard to the **title**,

   ☐ the text is approved as submitted by the applicant.

   ☒ the text has been established by this Authority to read as follows:

   COATINGS OF Mn+1AXn MATERIAL FOR ELECTRICAL CONTACT ELEMENTS.

5. With regard to the **abstract**,

   ☒ the text is approved as submitted by the applicant.

   ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

   a. the figure of the drawings to be published with the abstract is Figure No. 1A

   ☒ as suggested by the applicant.

   ☐ as selected by this Authority, because the applicant failed to suggest a figure.

   ☐ as selected by this Authority, because this figure better characterizes the invention.

   b. ☐ none of the figures is to be published with the abstract.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 2004/003390

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: H01R 13/03, H01R 39/20, H01R 41/00, C23C 30/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, H01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 03046247 A1 (ISBERG, PETER ET AL), 5 June 2003 (05.06.2003) -- | 1-59 |
| A | US 20020000598 A1 (SANG-BOM KANG ET AL), 3 January 2002 (03.01.2002), paragraphs 8-21 -- | 1-56 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 5 April 2005 | 19 -04- 2005 |
| Name and mailing address of the ISA/<br>Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Authorized officer<br>Nils Engnell/MP<br>Telephone No. +46 8 782 25 00 |

**INTERNATIONAL SEARCH REPORT**
Information on patent family members

01/03/2005

International application No.
PCT/IB 2004/003390

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